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We have generated and published signature curves for Sn, Se, Si, Ge and sulfur.

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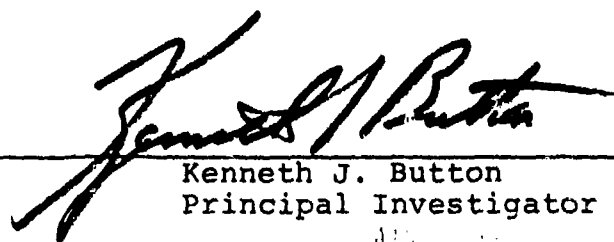
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Impurity and Defect Characterization in Epitaxial GaAs, InP
and the Ternary and Quaternary Compound Semiconductors

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IMPURITY AND DEFECT CHARACTERIZATION IN EPITAXIAL GaAs,
InP AND THE TERNARY AND QUATERNARY COMPOUND SEMICONDUCTORS

Kenneth J. Button, Principal Investigator

Introduction

A dual objective has been accomplished and is described in the enclosed preprint "Ultimate Method for Unambiguous Identification of All Donors in Epitaxial GaAs and Related Compounds." One aspect of the objective was to begin studies of specimens that have been prepared by the relatively new crystal growth technique, molecular beam epitaxy (mbe). The second aspect was to establish a method such that an individual species of donor could be identified positively without arousing the controversy among other observers that has characterized this type of investigation for the past 12 years. The method simply consists of the preparation of an mbe specimen of GaAs which would be strongly p-type

unless deliberately doped during growth with a single donor species. The doping with the tin (Sn) donor was minimal only to the extent necessary to render the epitaxial layer n-type. Thus the specimen was not highly compensated, $N_A/N_D = 0.4$, the only detectable donor being that of tin. Such a simple, one-spectral line specimen has not been observed by any diagnostic technique until this method was demonstrated.

Several vital modernization changes have been made in the equipment and in the data processing at no cost to this contract.

Specimens of high-purity epitaxial GaAs have been examined for many years in attempts to identify the chemical elements (the residual, unintentional impurities or imperfections) that act as donors or acceptors. The near infrared (or visible) photoluminescence technique has been more successful so far to identify impurities and complexes acting as acceptors. The far infrared photoconductivity technique, used here, has been more successful to identify impurities acting as donors. The photoconductivity technique has not earned a good reputation, however, because (a) it required extraordinarily high mobility specimens, and (b) the various investigators could not reproduce each other's results and could not agree on a number of the identifications. In our recent efforts to provide remedies to these problems, we have introduced several changes.

The New Method

The Signature Curve. This is nothing but the repeated measurement of the energy of the $1s \rightarrow 2p$ ($m = -1$) transition of a particular donor at several intensities of applied magnetic field. This accomplishes several things: It establishes a "signature curve" for that donor so that if we (or others) ever observe that transition at any value of magnetic field, that point must fall on the signature curve; if not, it does not represent the same donor. A recent example is our doping of mbe p-type GaAs with the donor tin (Sn) and our subsequent generation of the first signature curve for tin. It had the same shape as our other donor signature curves but displaced slightly in energy. We then referred to the literature and found an identification of tin by Fetterman, et al. in 1972 at 0.573 Teslas with an energy corresponding to a frequency of 35.65 cm^{-1} . That point fell on our signature curve for tin, accurate to four significant figures. No controversy.

High Intensity Magnetic Fields. At the M.I.T. National Magnet Laboratory, field intensities up to 20 Teslas have been available to visiting scientists at no cost since 1962. It has also been known that the application of a high intensity field improves resolution of closely spaced spectral lines by acting on the $1s$ wave function to (a) separate the lines and (b) narrow the lines. But we were able to demonstrate a fact of much greater fundamental

significance, namely, that the magnetic field produces an extraordinarily large change in the line shape of the $1s \rightarrow 2p$ ($m = -1$) transition. It was accepted that the transition was hydrogen-like but that the line shape, having a sharp edge on the high energy side and a long "tail" on the low energy side was not hydrogen-like. We showed that the long "tail" is gradually suppressed as the magnetic field intensity is increased which is not accounted for by the 1973 established theory of Stark broadening.

Transmutation Doping. Shortly before we began our studies, other investigators mistakenly identified tin (Sn) as selenium (Se). This is understandable because the observation was made at a different energy of $1s \rightarrow 2p$ ($m = -1$) in a different magnetic field intensity than that used by Fetterman, et al. who correctly identified tin at one point in 1972. Since signature curves had never been established, the error could not be detected. But the simple remedy is neutron irradiation to produce the reaction: $As + n \rightarrow Ge + e^-$ and found their "carbon point" on our germanium signature curve. This identification was not accepted at face value and the original erroneous carbon identification is simply considered to be challenged. We predict that carbon, being amphoteric, enters the arsenic site as an acceptor and does not enter the gallium site as a donor in sufficient quantity ever to be observed as a donor by any technique now known.

The Single Donor Spectrum. The signature curve for a donor can be established most decisively and the line shape can be studied most accurately if the photoconductivity spectrum for a particular specimen contains only one photoconductivity peak for a single, known donor dopant. The method of doping mbe p-type GaAs with a single donor was described in the Introduction and in the attached preprint.

Conclusion

All of the remedies described in the previous section, "The New Methods," have been available to previous investigators since activity began in the far infrared photoconductivity method 12 years ago. They have not been used and are not now being used. We propose to establish and verify signature curves, one at a time, for all possible chemical species which can be introduced as donors by molecular beam epitaxy. The method of "single donor spectrum" will be used for GaAs and for all related compounds for which suitable variations in the method can be devised. Collaborative relationships will be cultivated with scientists familiar with the molecular beam epitaxy technique of crystal growth.

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ULTIMATE METHOD FOR UNAMBIGUOUS IDENTIFICATION
OF ALL DONORS IN EPITAXIAL GaAs AND RELATED COMPOUNDS*

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When epitaxial GaAs is grown by the method of molecular beam epitaxy (mbe) it would be p-type unless it is intentionally doped lightly during growth by using a particular substitutional donor atom. We have chosen the tin donor in this case to render the specimen n-type. Then the conventional far infrared photoconductivity technique is used to observe the 1s to 2p transition of the electron of the tin donor. The identity of the donor, the energy of the quantum transition as a function of applied magnetic field intensity, and the line shape characteristics of that particular donor then become unquestionable..

Key Words: semiconductors, epitaxial GaAs, impurities in semiconductors, molecular beam epitaxy.

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Introduction

Far infrared photoconductivity of epitaxial n-GaAs at low temperature has been used for many years to identify some of the residual donors by using the photon transition $1s$ to $2p$ with subsequent thermal excitation of the donor electron to the conduction band. The central cell correction (chemical shift) for the large variety of donors is so small that the $1s$ to $2p$ spectral line position, line shape and donor identity can hardly be resolved. This paper illustrates the solution to that problem by giving data on the tin donor line standing alone in the spectrum with no other donor lines present. This permits the study of the line position and shape as a function of magnetic field and also establishes the unambiguous identification of the donor species. This is accomplished quite simply by applying the same high magnetic field photoconductivity method to a specimen prepared not by liquid or vapor phase epitaxy but by molecular beam epitaxy (mbe), which is normally p-type but to which a minimum amount of tin donors have been deliberately added to convert the layer to n-type. Then there is only one donor line observed, that of tin, and the line shape can be studied without resort to deduction or speculation.

Other mbe n-type epitaxial specimens can be prepared which contain a single donor species. Tin is the most convenient species to be used to illustrate the initial disclosure of this new method which solves our previous difficulties from which we have suffered for so many years. The first strong point is established by the fact that tin was precisely identified and located in a high purity vpe specimen that was back-doped with tin by Fetterman, Waldman, Wolfe, Stillman and Parker (1) in 1972. Our "signature curve" (2,3) for tin shown in Fig. 1 intercepts the single point of Fetterman, et al. precisely at their values of $H = 6.573$ Teslas and frequency of 35.65 cm^{-1} from their optically pumped NH_3 laser. Thus we are clearly dealing with the tin donor and we avoid, so far, the controversy that has characterized this type of investigation.

Characteristic Line Shape

A second strong point needs to be established, namely, that the hydrogen-like transition $1s$ to $2p$ ($m = -1$) of the

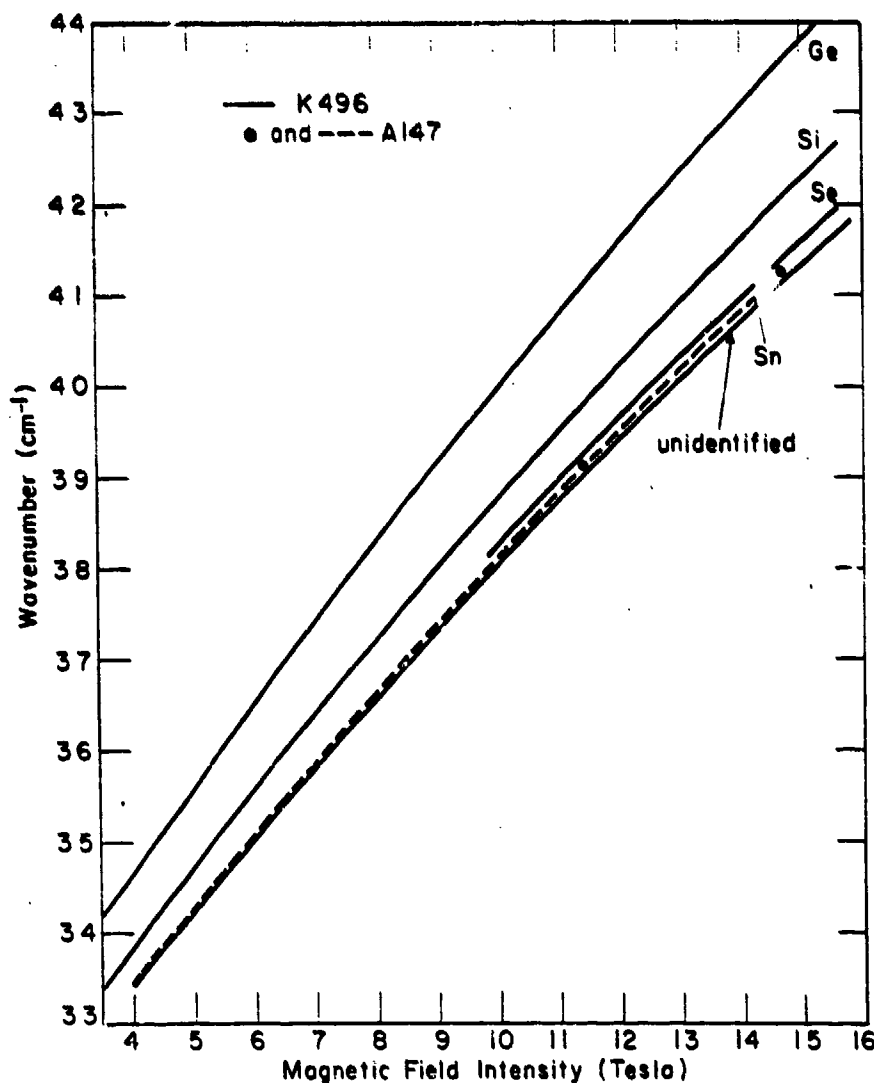


Figure 1. The "signature curves" generated by plotting the energy of the 1s 2p ($m = -1$) transition energy for different values of applied magnetic field intensity. This procedure has been adopted recently to assure that each donor is correctly identified and also to permit the precise comparison of the data of various experimenters. For example, the identification of Sn by Fetterman et al. (1) in 1972 falls precisely on the signature curve for Sn in Fig. 1 above, correct to four significant figures both in wave number and magnetic field intensity. This should not be surprising, in principle, but events such as this are rare in this literature.

donor electron exhibits an extreme asymmetry in the line shape. Such an asymmetry is not hydrogen-like, of course. The asymmetry is best observed in the absence of an applied magnetic field or, at least, in a magnetic field of less than 5 Teslas (3,4). The asymmetric transition line has a very sharp edge on the high frequency side and a very long "tail" on the low frequency side. This was discussed by Korn and Larsen (5) in 1973. It was recently demonstrated (3,4) that this long low-frequency tail is gradually suppressed as the applied magnetic field is increased to values above 5 T. The characteristic low field line shape was not noticeable in the early 1970 recorder traces of the spectra of several donors published by Fetterman, Larsen, Stillman, Tannenwald and Waldman (6) but careful plotting of their data by Korn and Larsen (5) revealed the sharp high field edge and the long low field tail very clearly and their theoretical calculations based upon the Stark effect fit the experimental plots very satisfactorily at least up to 10 T which was the highest field used.

The characteristic line shape is never seen in a deliberately back-doped vpe n-GaAs specimen apparently because of the severe line broadening of excessive doping which can hardly be avoided. One of the clearest illustrations of this is the tin doped specimen used by Fetterman, et al. (1) in 1972.

The Single Line Spectrum

Figure 2 shows an example of the single line spectrum of the tin doped specimen. It was prepared by molecular beam epitaxy by one of us (A.Y. Cho). The study of this line as a function of magnetic field is much less complicated than those examples given in the recent review paper by Stillman, Wolfe and Korn (7) from which Fig. 3 was copied. Here we see that Sample #3 shows four lines each exhibiting the characteristic line shapes while Sample #2 does not. Sample #2 is Lincoln Laboratory #B4-21A. It has the remarkably high mobility of $207,000 \text{ cm}^2/\text{V-sec}$ at 77 K and is not deliberately doped. The four donors of B4-21A (#2 in Fig. 3) were identified in the original reference (7) as (left to right) a gallium vacancy, tin, silicon and carbon. When the same specimen B4-21A was studied more recently (3,4), the identification was established differently. The second line is selenium, not tin, and the fourth line is

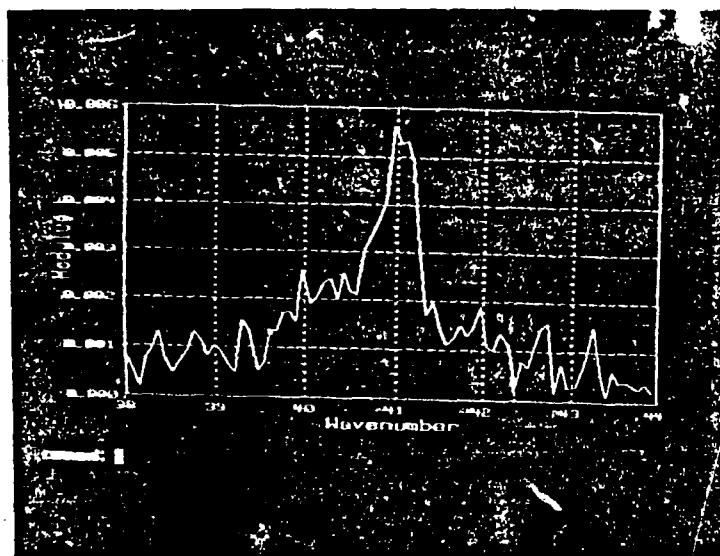


Figure 2. Photograph of photoconductivity signal at 7 K for the hydrogen-like $1s \rightarrow 2p$ ($m = -1$) transition of the donor electron of tin in epitaxial GaAs, in an applied magnetic field of 14.3 Teslas. The high field has nearly quenched the long "tail" on the left hand side of the spectral line but a vestige of the asymmetry of the line is still noticeable. It is only possible to restrict the spectrum to one donor by growing the epilayer using molecular beam epitaxy while introducing a small amount of a single donor element during growth. The spectrometer resolution is 0.06 cm^{-1} . The mobility of the specimen is $\mu_{300} = 8080$ ($\mu_{77} = 105,000$) $\text{cm}^2/\text{V-sec.}$ for $N_D - N_A = 4 \times 10^{14}/\text{cm}^3$ and $N_A/N_D = 0.4$.

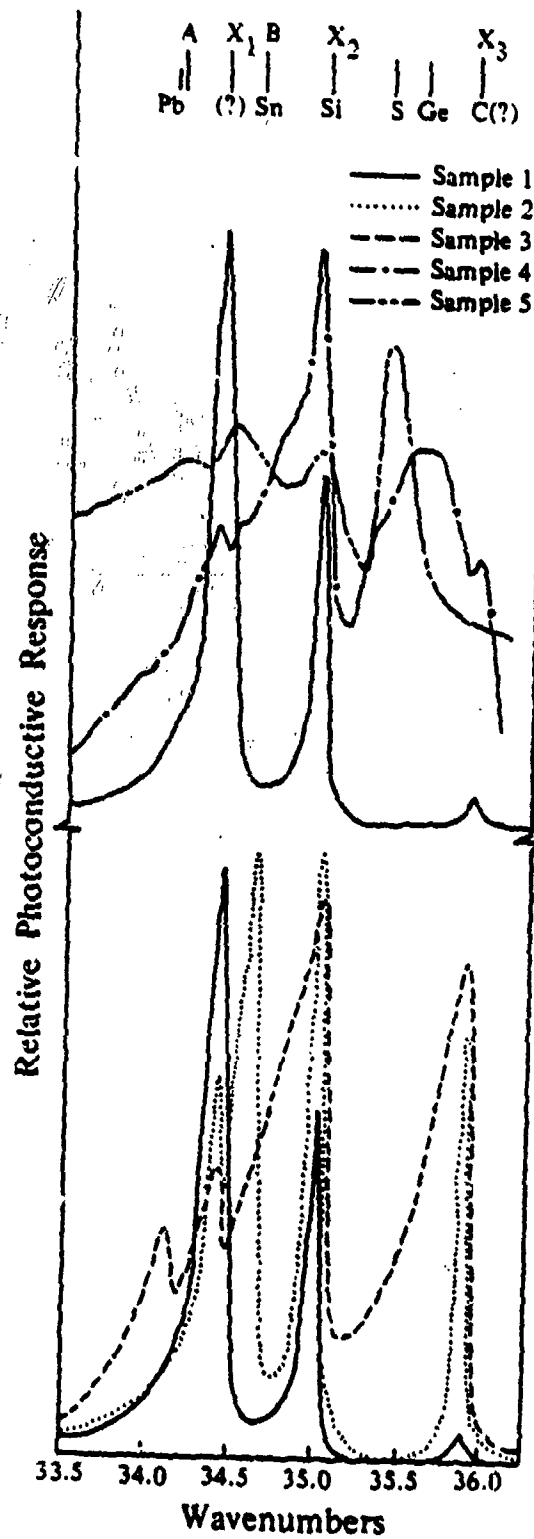


Fig. 3. Photograph from reference 7 showing comparative photoconductivity signals from several unintentionally doped, very high quality vpe epitaxial GaAs specimens. The text in this reference states that the data was taken at "about 50 kG."

germanium, not carbon. Figure 1 shows how difficult it is to distinguish selenium, tin and the unidentified (Ga vacancy) lines when there are so many lines in the same spectrum. The fact that X_3 is actually germanium, not carbon, has been confirmed by Reynolds and Litton (3).

It appears that the new approach suggested here of introducing only one donor into an mbe specimen that would ordinarily be p-type, if undoped, may clear up some of the problems associated with the difficult task of interpreting complicated spectra and inconsistent line shapes.

Identification of Other Donors

It appears that all donors can now be identified, one at a time, by introducing a very small quantity of the single donor into the growth of an epitaxial specimen prepared by the method of molecular beam epitaxy. Donors should be identified soon in GaAs, InP, and the ternary and quaternary compounds as rapidly as the specimens can be prepared.

Substitutional Donors

The Group IV elements, Pb, Sn, Ge, Si and C are amphoteric. They act as donors when substituted on the Ga site or as acceptors when substituted on the As site. This is particularly true of carbon because previous experiments designed to observe the carbon donor have been inconclusive. There is no dispute concerning silicon because it is a persistent donor in all specimens that have previously been grown in quartz vessels. Germanium has been identified by transmutation doping (neutron irradiation) as described in reference 3, Fig. 2 and reference 4, Fig. 7. It has also been confirmed by Reynolds and Litton (8). The observation of the Pb donor has not been confirmed experimentally.

The persistent contaminants of the Group VIA elements are Te, Se, S and oxygen. Tellurium has not been reported but Se and Sn have been mistaken for each other. Figure 1 illustrates the possible difficulty that may be encountered to resolve Se, Sn and the unidentified line, particularly if one does not generate a signature curve but relies on only one point which has been the common practice in the past. This shows the need to develop a method for absolute, unambiguous identification as in the present

case for tin. Indeed, it was presumed that Se (and Ge) had been identified absolutely and unambiguously by means of neutron transmutation of Ga to Ge and As to Se, but these identifications are still not accepted by everyone. Sulfur has generated the clearest, definitive disagreement of all. There is simply total disagreement. Previous researchers insist that sulfur lies between germanium and silicon in Fig. 1, but McCoy (2) prepared a sulfur doped specimen by the vapor phase epitaxial method and we found a clearly resolved signature curve at an energy below the unidentified line in Fig. 1 where it has been claimed Pb should appear. If possible, the next mbe specimen should be sulfur doped GaAs.

Transmutation Doping

We originally intended to obtain an ordinary mbe specimen, which would naturally be p-type, and turn it into n-type by transmuting in a nuclear reactor. This will be done as soon as a high mobility virgin specimen becomes available.

The Unidentified Donor

The signature curve for the unidentified donor shows that it is indeed a simple hydrogen-like substitutional donor. Until the signature curve (Fig. 1) was developed recently (2), several excellent speculations have been discussed. Since it appears only in vpe specimens of GaAs, and it always appears in vpe specimens of GaAs, it can hardly be a common chemical contaminant. It did not appear in the present Sn doped mbe specimen, of course. Although we shall continue to pursue the identity of this mysterious donor, it is no longer of primary importance. The mbe method disclosed here should dominate investigations of binary, ternary and quaternary compounds.

Conclusions

The new method of employing mbe epitaxial GaAs (p-type) lightly doped with a single type of donor now provides the long-sought solution to the problem of resolving and identifying the variety of possible substitutional donors, one at a time. Additional mbe specimens, each lightly doped with its own single donor, will soon furnish us with the complete list of donor identifications

which has been pursued for more than a decade.

Acknowledgments

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